Polydiacetylene Organic Semiconductors

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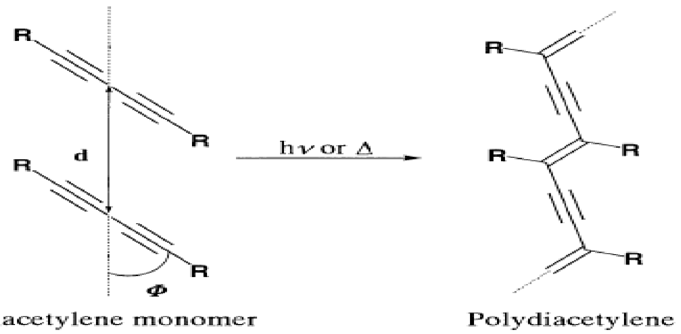
Polydiacetylene chemistry began when G. Wegner in 1969 explained that conjugated diacetylenes when arranged in the right way in a crystal lattice, would polymerize with heat or UV radiation, usually to a deep blue unsaturated conjugated polymer.

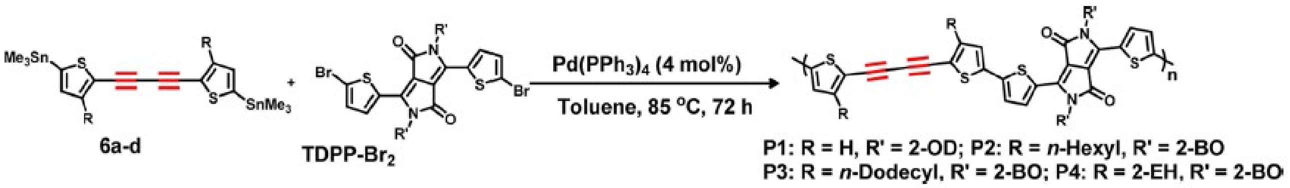
Polydiacetylenes. Springer, Berlin, Heidelberg, 1984. (This is probably the best early review.)



Scheme 1. Polymerization scheme of DA monomers. When the condition for monomer array in solid state is satisfied, where the distance *d* and angle *Φ* are about 5 Å and 45°, polymerization occurs at 1,4-position to give PDA.

Matsuzawa, Hiroshi, et al. "Synthesis of polydiacetylenes from novel monomers having two diacetylene units linked by an arylene group."*Polymer journal",* 33.2 (2001): 182.

Recently Marks et. al. revealed diacetylene containing donor organic semiconductors.



"Additionally, the synthesis and study of diacetylene-containing polymers is a valuable step toward a new materials family with a potentially rich postfabrication functionalization chemistry. Postfilm deposition topochemical polymerization, in particular, could yield new platforms for two-dimensional (2D) π-conjugated organic semiconductors.”

Eckstein, Brian J., et al. "Buta-1, 3-diyne-based π-conjugated polymers for organic transistors and solar cells."*Macromolecules”,* 50.4 (2017): 1430-1441.

Also with similar ideas:

Yue, W., Zhen, Y., Li, Y., Jiang, W., Lv, A., & Wang, Z. (2010). One-pot synthesis of well-defined oligo-butadiynylene-naphthalene diimides.*Organic letters*, *12*(15), 3460-3463.

Kang, H., Jiang, W., & Wang, Z. (2013). Construction of well-defined butadiynylene-linked perylene bisimide arrays via cross-coupling.*Dyes and Pigments*, *97*(1), 244-249.

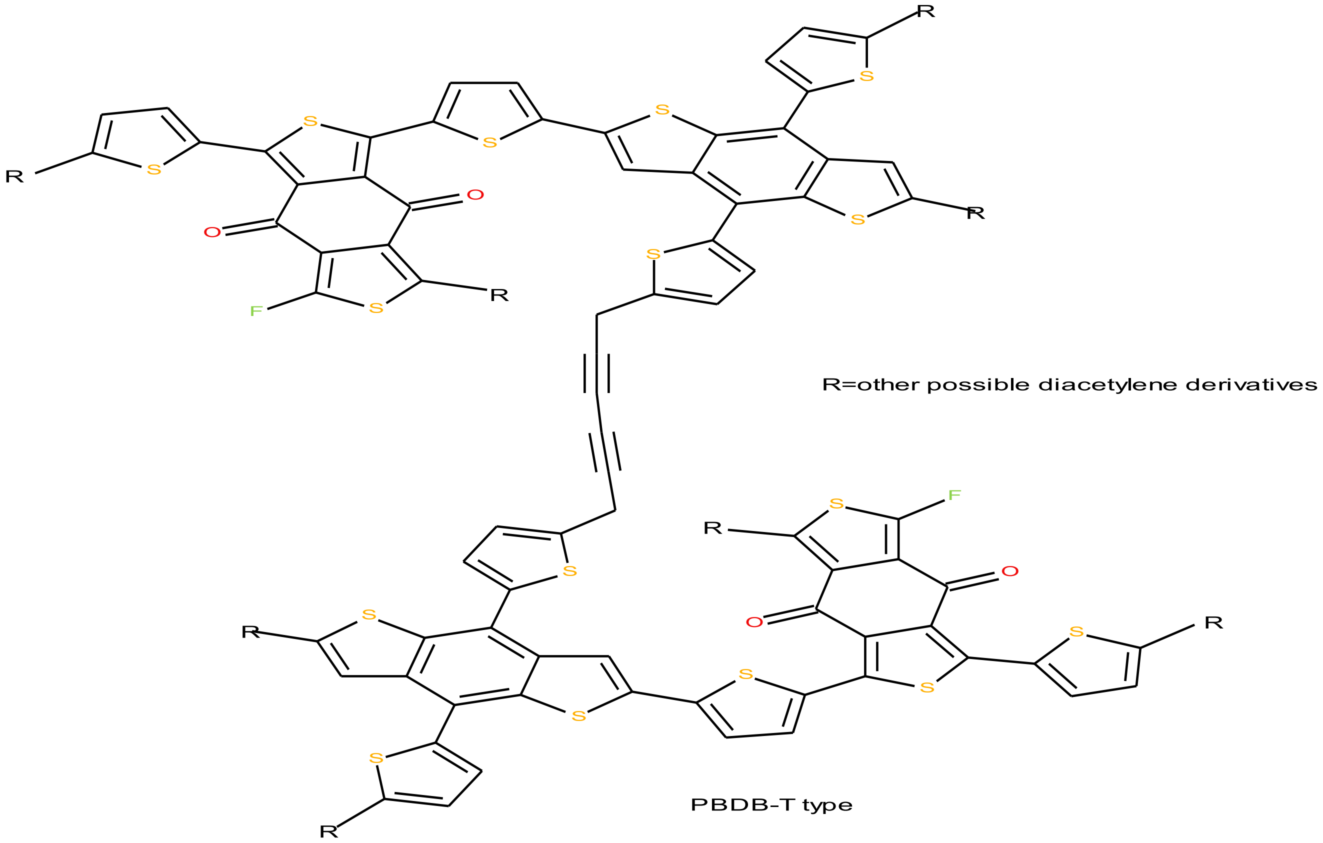
However, these references do not indicate that the above diacetylenes were successfully polymerized to PDA's! However, I'm sure these scientists were or are actively working on this idea?

Proposals:

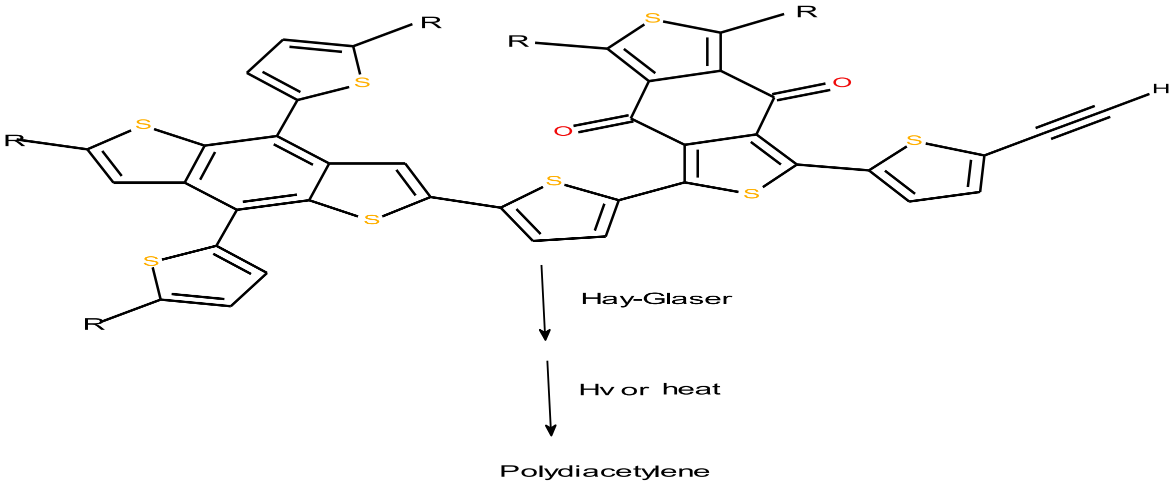
My idea is to derivatize donors or acceptors with diacetylenes and to perform the topochemical polymerization of said diacetylenes post mixing. This might solve one of the problems that I believe occurs with OSC's because polymeric donors are not adequately mixable with NFA A-D-A's. It is difficult to mix polymers with small compounds. Mixing monomeric donors with monomeric acceptors would result in many more bulk heterojunctions(BHJ) after subsequent polymerization. This would hopefully result in higher Voc and fill factors because exitons which are known to dissociate to free electrons and holes at the interface of BHJ would have more BHJ's to improve this activity.

Polymerization of the diacetylene derivatives could be accomplished by either heating(annealing) or UV radiation. Donors as small compounds might very easily form crystalline regions that would result in the necessary morphology for topochemical formation of PDA's. PDA's would afford another conjugated pathway for rapid movement of holes while the increased heterojunctions, would afford more opportunity for the CTS exitons to dissociate into free electrons and holes. As an added benefit, PDA's can have small band gaps and could enhance photon absorption.

Derivatizing donors with diacetylenes is apparently straight forward.



Scheme 1: This shows a diacetylene at one possible position of a monomeric PBDB-T donor. The resulting PDA would be decorated with donors as side groups. The R groups are there to indicate typical donor derivatives but they are there to show other possible sites for diacetylene coupling.



Scheme 2: Alternate diacetylene polymeric derivative. Obviously, the acetylene can derivatize other positions and if a two acetylenes are attached then Hay-Glaser coupling will afford polydiacetylenes.

So what I'm indicating is that the position of the diacetylenes might require experimentation as they can be at several locations on typical donor monomers. The downside to this concept is that the stringent requirements concerning the morphology of the solid diacetylene usually as a crystalline compound is not met by every diacetylene containing compound. Diacetylene-containing A-D-A and (polymeric) donor compounds from my understanding don't seem ideal for forming PDA's because they might not crystallize appropriately.

"About 40 years ago, Wegner discovered that the 1,4-diacetylene polymerization could take place in the solid state via a topochemical reaction. If the reactive monomers are preorganized at a distance commensurate with the repeat distance in the final polymer, then the application of thermal or photochemical energy can bring about the polymerization, This preorganization occurs fortuitously for some crystalline diacetylenes, but it is neither a reliable nor a general means of synthesis. The vast majority of diacetylene monomers crystallize in some other manner incommensurate with their corresponding polymer, so no polymerization occurs, and the corresponding polymer remains unknown."

Lauher, Joseph W., Frank W. Fowler, and Nancy S. Goroff. "Single-crystal-to-single-crystal topochemical polymerizations by design."*Accounts of chemical research"*, 41.9 (2008): 1215-1229.

“The typical topochemical requirements for diacetylene polymerization in crystalline state are known to be as follows:

The monomers need to be spaced ~4.9 Å apart, a separation equal to the repeat distance in the corresponding polymer. An angle between the axis of the array and the diacetylene rod of 45 ° will bring the C1 and C4 reactive centers of neighboring diacetylenes into a van der Waals contact of 3.5 Å.”

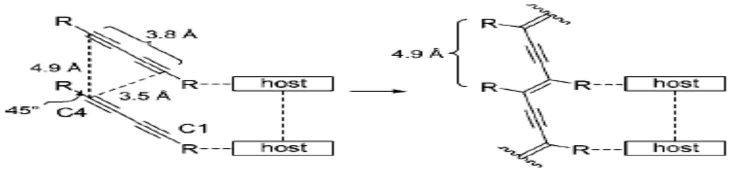


Figure 1. Topochemical requirements for diacetylene polymerization and the host—guest strategy of aligning diacetylenes for such requirements.

Li, Zhong, Frank W. Fowler, and Joseph W. Lauher. "Weak interactions dominating the supramolecular self-assembly in a salt: a designed single-crystal-to-single-crystal topochemical polymerization of a terminal aryldiacetylene."*Journal of the American Chemical Society”,* 131.2 (2008): 634-643.

The above reference not only illustrates the requirements for topochemical polymerization but a way around those diacetylenes that do not or are difficult to polymerize by connecting them to another compound(host) that by H-bonding arranges them in the proper morphology for polymerization.

PDA's can not be prepared in solution as 1,2 and 1,4 reactions amongst others will occur. Only as appropriate crystalline morphology will they polymerize. So it might very well be wishful thinking that by placing diacetylene functionality on a donor and/or acceptor, organic semiconductors that they would form PDA's after film formation during annealing, for example.

Also the vast number of PDA references left me searching as I could not find anything recently concerning organic semiconductors except for the recent mention in the T. Marks (above) reference.

Several references however struck me as a way around the problem of correct morphology in a film that could have crystalline regions more likely to form PDA's. These are the references to self-assembled macrocyclic diacetylenes (MCDA).

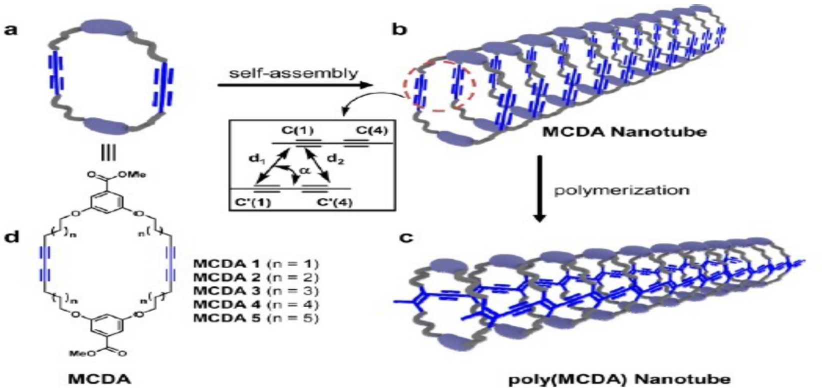


Figure 1. A polydiacetylene nanotube from a macrocyclic diacetylene (MCDA). (a) Schematic representation of a MCDA. (b) Nanotube from self-assembly of MCDAs. (c) Topochemical polymerization of a MCDA nanotube results in formation of a polydiacetylene (PDA) nanotube. Geometric parameters for topochemical polymerization of DAs are d_1 (repeat distance), d_2 (contact distance), and α (tilt angle). Optimal values (d_1 = 4.9 Å, d_2 = 3.5 Å, and α = 45°). (d) Structure of MCDAs investigated for tubular PDA formation.

Heo, Jung-Moo, et al. "Chromogenic Tubular Polydiacetylenes from Topochemical Polymerization of Self-Assembled Macrocyclic Diacetylenes."*Macromolecules*”, 50.3 (2017): 900-913.

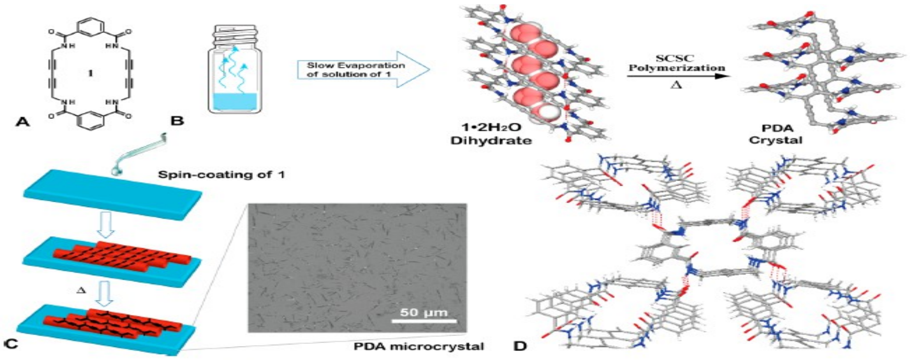


Figure 1. Diacetylene macrocycle 1 assembles from solution. (A) Molecular structure of 1. (B) The dihydrate $1\cdot 2H_2O$ can be polymerized in a SCSC process to give a PDA crystal. (C) PDA microcrystal generated by spin-coating a 1.0 mg/mL macrocycle 1 solution on the Si wafer followed by thermal treatment (190 °C for 3 h) to induce the polymerization. (D) Individual PDA nanotubes are connected through amide bonds to four neighboring nanotubes.

Xu, Weiwei L., et al. "Single crystal to single crystal polymerization of a self-assembled diacetylene macrocycle affords columnar polydiacetylenes."*Crystal Growth & Design”,* 14.3 (2014): 993-1002.

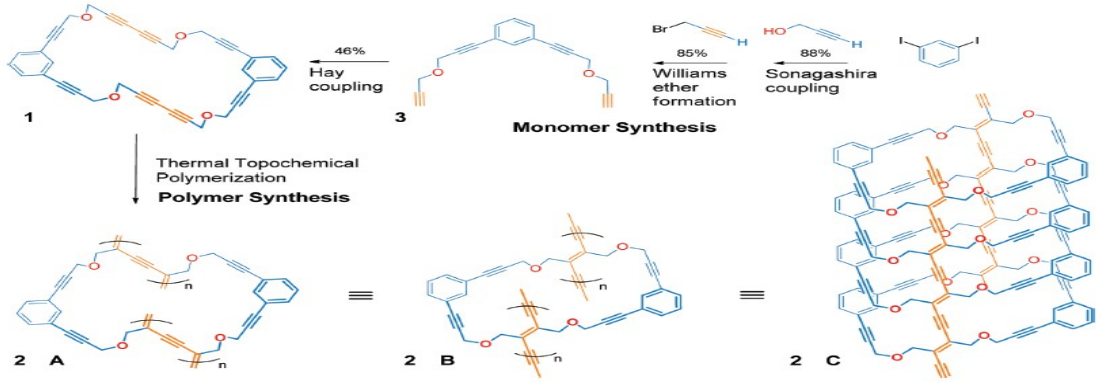
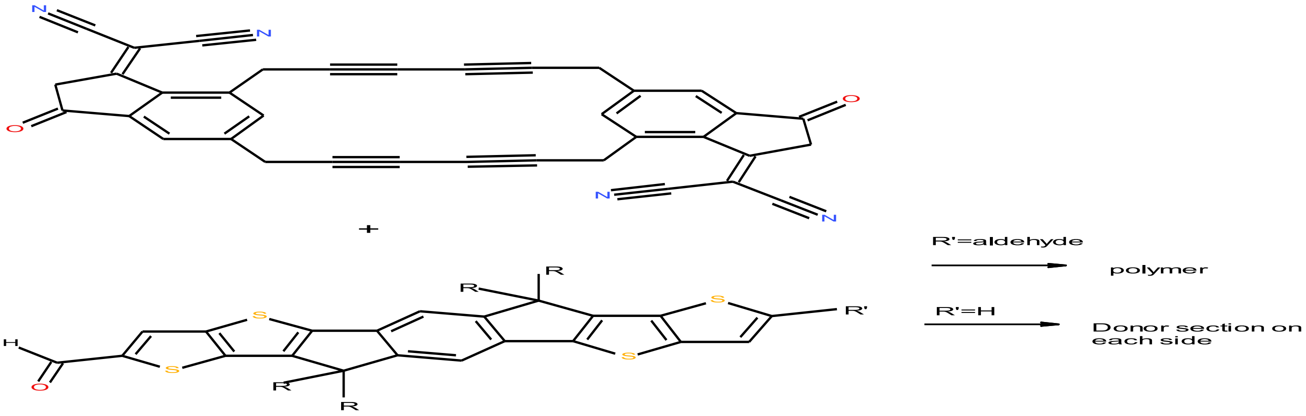


Figure 2. Synthesis of macrocycle 1 from readily available reagents. In the crystalline state, the compound undergoes a topochemical polymerization to give the tubular polymer 2. Drawing 2 A shows the original 34-atom macrocycle as it appears embedded within the polymer. After polymerization, a new and smaller 30- atom macrocycle 2 B can also be identified. The final drawing 2 C should be compared to the actual structure determined by single-crystal X-ray diffraction (Figure 3D).

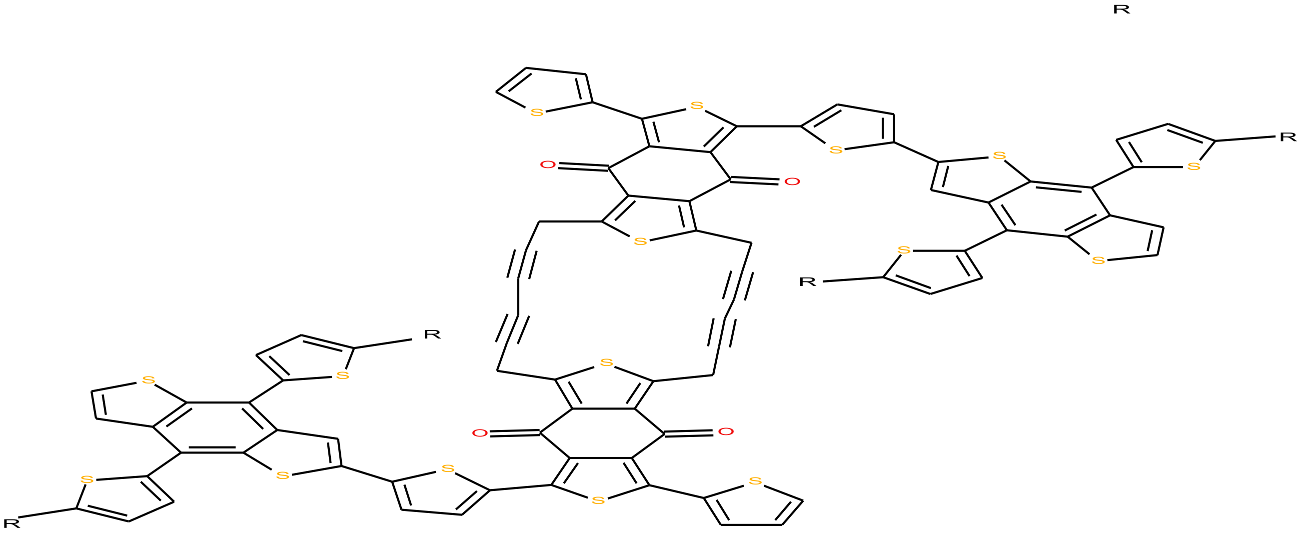
Hsu, Te-Jung, Frank W. Fowler, and Joseph W. Lauher. "Preparation and structure of a tubular addition polymer: a true synthetic nanotube."*Journal of the American Chemical Society*”, 134.1 (2011): 142-145.

Xu, Yuewen, et al. "Thermal reaction of a columnar assembled diacetylene macrocycle."*Journal of the American Chemical Society*”, 132.15 (2010): 5334-5335.

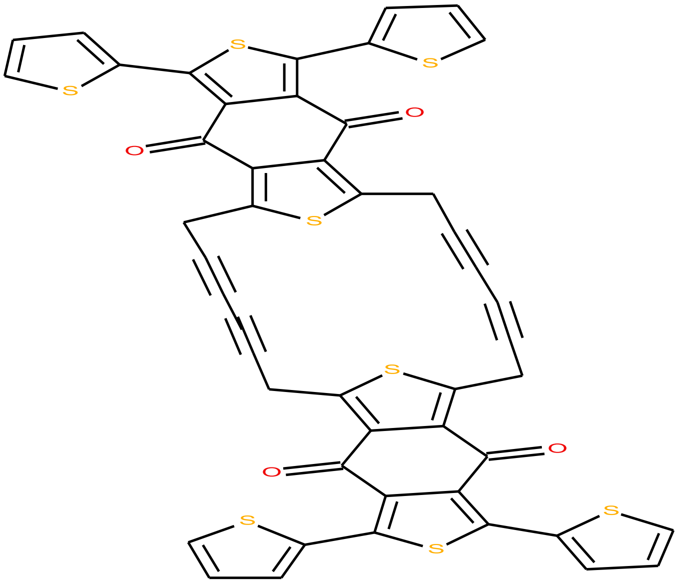
The above references(not an exhaustive list) indicate that symmetrical macrocyclic diacetylenes more readily form polymerizable crystalline structures vs. non-cyclics and are polymerizable by UV or heat. This led me to the following idea:



Scheme 3: PDA A-D-A NFA...The R groups are the typical structures found in A-D-A NFA's. Note that the resulting PDA's are not directly conjugated with the aromatic groups. I did this because the above reference examples don't show conjugation.

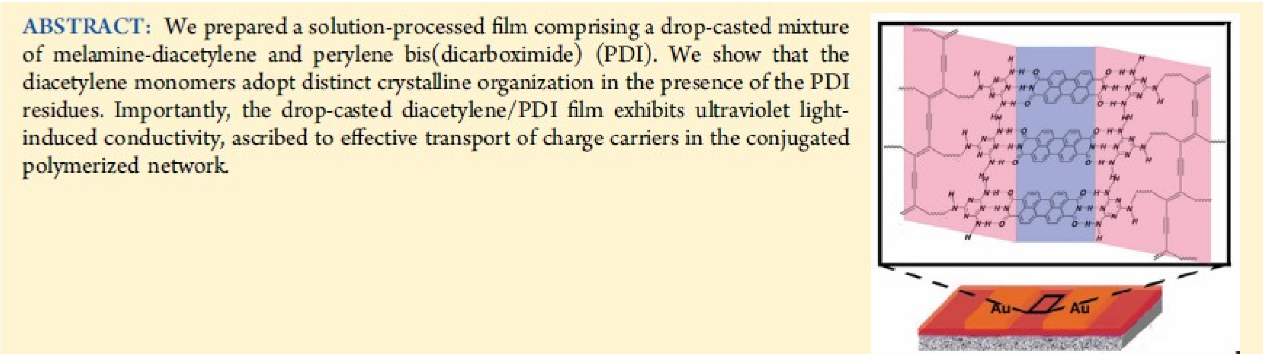


Scheme 4: PDA donor monomer. This assumes that this monomer forms a suitable crystalline structure. If not a more symmetrical donor might work.



Scheme 5: Can the PDA's unsaturation enhance the movement of exitons in this structure? Exitons are known to jump across barriers.

The PDA is not conjugated with the donor but the literature indicates that electrons generated in the donor or acceptor can be conducted in the PDA even though it is not conjugated with these structures. For example:

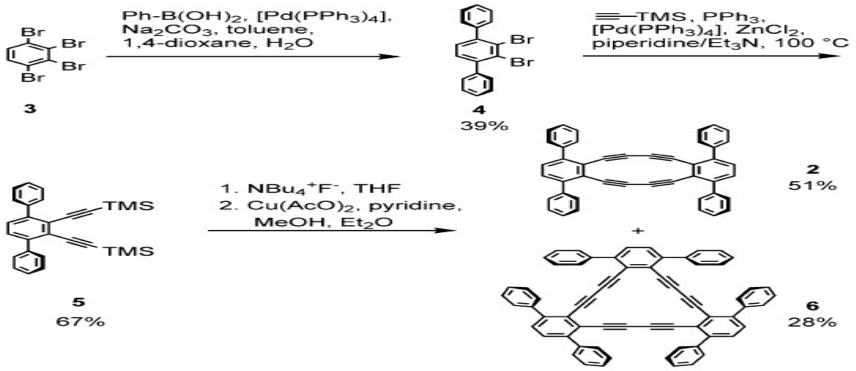


ABSTRACT: We prepared a solution-processed film comprising a drop-casted mixture of melamine-diacetylene and perylene bis(dicarboximide) (PDI). We show that the diacetylene monomers adopt distinct crystalline organization in the presence of the PDI residues. Importantly, the drop-casted diacetylene/PDI film exhibits ultraviolet light-induced conductivity, ascribed to effective transport of charge carriers in the conjugated polymerized network.

Jiang, Hao, et al. "Light-induced conductivity in a solution-processed film of polydiacetylene and perylene diimide."*The Journal of Physical Chemistry Letters",* 7.9 (2016): 1628-1631.

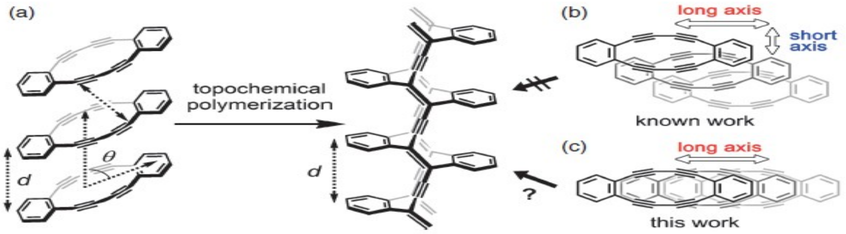
Should conjugation be necessary, then the following should be considered:
It is possible to couple diacetylenes directly to benzene and presumably other aromatics.

I. Hisaki et al. *Bull. Chem. Soc. Jpn. Vol. 87, No. 2 (2014)*

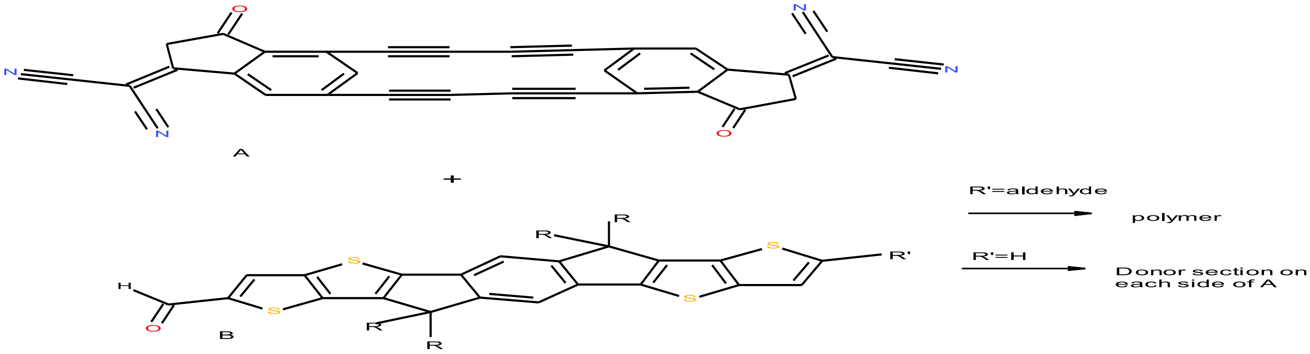


Scheme 2. Synthetic route of [12]DBA **2**.

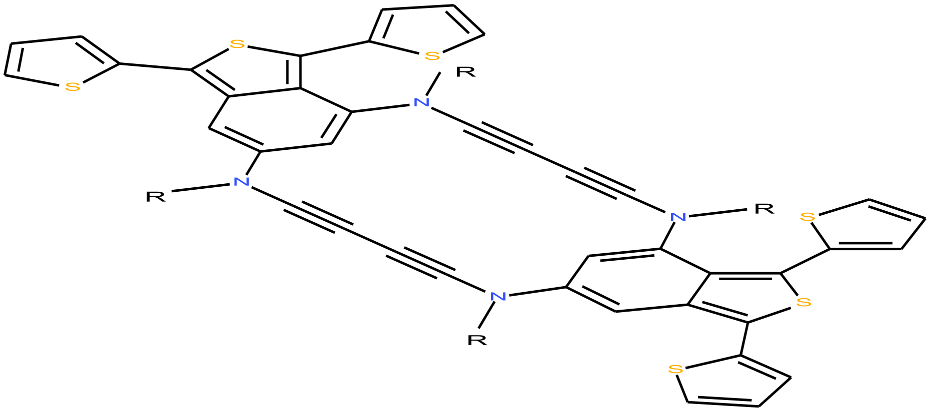
I. Hisaki et al. *Bull. Chem. Soc. Jpn. Vol. 87, No. 2 (2014)* 329



Scheme 3. (a) Proposed ene–yne ladder polymer formed by topochemical polymerization of [12]DBA. Stacking manner of [12]DBA with slippage both in short and long axes directions (b) and only in long axis direction (c).



Scheme 6: “A” is shown with meta substitution but ortho is possible.



Scheme 7: Conjugation is through the free pair of electrons on nitogen. The following reference lends credence to this concept.

“we designed the novel diacetylene monomer 1 as shown in Fig. 2(a), where N,N phenylenediamine unit was introduced as a conjugated linker.
Since phenylenediamines (PDs) are well-known to be electrodonors, the linker should contribute to the decrease in the ionization potential.”

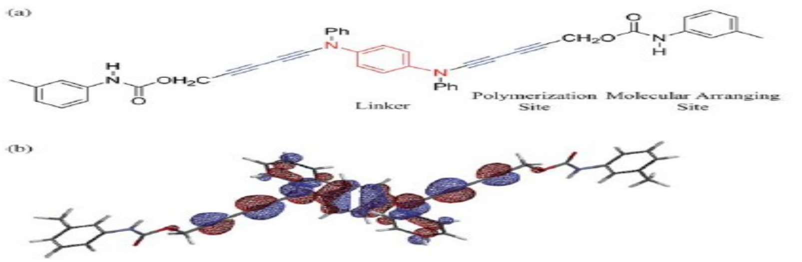
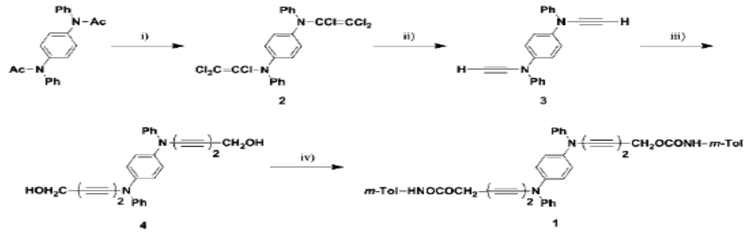


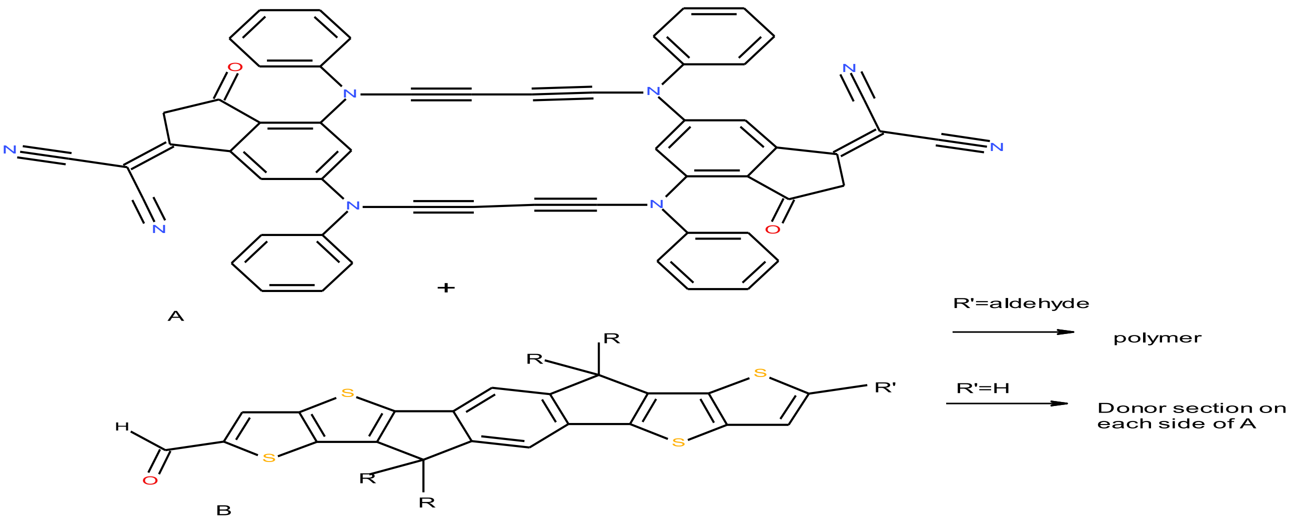
Fig. 2 (a) Molecular design of the diacetylene monomer as a building block of a conjugated ladder polymer (b) HOMO of the monomer 1 obtained by DFT calculation, where its energy level of HOMO is estimated to be −5.2 eV.

Tabata, Hideyuki, et al. "Preparation and properties of two-legged ladder polymers based on polydiacetylenes."*Journal of Materials Chemistry”,* 22.1 (2012): 115-122.

Tabata et. al. synthesis:



Scheme 1 Preparation of the monomer **1**. (i) PCl_5, toluene, 55% (ii) *n*-BuLi, THF, 50% (iii) 2-propyn-1-ol, O_2, CuCl, TMEDA, acetone, 50% (iv) *m*-TolNCO, THF, 61%.



Scheme 8: Another conjugated versions of scheme 3. Note(here and above) there are two possible isomers of A, cis and trans.

This proposal suggests that structures of compounds that are active as donors or acceptors (p or n type semiconductors) can be attached to diacetylenes that can be polymerized to PDA's. Such PDA's are excellent charge carriers either by themselves or doped. In organic solar cells, such diacetylenes can form crystalline regions that will undergo topochemical polymerization and afford more BHJ's and active charge transport thus increasing the resulting PCE's.

Organic semiconductors are a very active research area with numerous references appearing daily. I believe that OSC's will eventually win the race to commercialization. After all the Sun is a powerful source of clean energy but a safe inexpensive solar cell with acceptable efficiency and cost is needed. I hope the above ideas might be of some value.

Thank you for reading this proposal!
Dr. Robert B. Login   rloginconsulting.com